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Fabrication and characterization of energy storing supercapacitor devices using coconut shell based activated charcoal electrode

Amrita Jain, S.K. Tripathi*

Department of Physics, Jaypee University of Engineering and Technology, AB Road, Raghogarh 473226, Guna, Madhya Pradesh, India

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ABSTRACT

In the present studies coconut shell based treated activated charcoal (CST) was synthesized by chemical activation method using KOH (potassium hydroxide) as an activating agent. Surface area analysis shows that CST has mesopores of size 3 nm having specific surface area of 1640 $m^2 g^{-1}$. Electrochemical double layer capacitor (EDLC) was fabricated using CST as an electrode material with blend polymer electrolyte having specific capacitance of 534 mF cm^{-2} (equivalent to single electrode specific capacitance of 356.2 F g^{-1}). The corresponding energy and power density of 88.8 Wh kg^{-1} and 1.63 kW kg^{-1}, respectively, were achieved for EDLC.

1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors or ultracapacitors, are energy-storage devices which deliver 100 times the power of batteries and are able to store 10,000 times more energy as compared to conventional capacitors [1–4]. Supercapacitor stores energy by forming a double layer of electrolyte ions on the surface of conductive electrodes. It is not limited by the electrochemical charge transfer kinetics of batteries and hence it can operate at very high charge and discharge rates and have a lifetime of over a million of cycles [5,6]. At present, the energy stored in supercapacitors is lower than that of batteries, which restricts their adoption to the applications that require high life cycle and power density. Therefore ample of efforts have been made to explore electrode materials for supercapacitor applications [7–9].

Among the diverse options, activated carbons are commercially used as an electrode material for the EDLC application because of their high surface area, favorable pore size distribution and good electrical conductivity. Activated carbon is an attractive option because of its abundance, cost effective and environment friendly in nature [10]. The high specific surface area and porosity is the key advantage of activated carbon to form an effective double layer, which is characteristic of supercapacitors with high power density. It may be noted that activated carbon from biomass is a natural and renewable one and its synthesis process is completely eco-friendly. Biomass may be converted into carbon by controlled thermal decomposition. The steps involved in the conversion of biomass to carbon are: (1) up to 150 °C desorption of adsorbed water takes place, (2) splitting up of matter structure and water between 150 °C and 260 °C, (3) chain scissions or depolymerization and breaking of C—O and C—C bonds within ring units releasing water, CO and CO_2 between 260 °C and 400 °C, (4) aromatization forming graphitic layers above 400 °C and (5) above 800 °C, thermal induced decomposition and the rearrangement reaction are almost terminated leaving behind a carbon template structure. The systematic order of breaking down of main components of biomass is: 200–800 °C (hemicellulose), 260–350 °C (cellulose) and 280–500 °C (lignin). 80% of the total weight loss takes place between 260 °C and 400 °C, which may vary between 40% lignin to about 80% cellulose because of the evolution of H_2O, CO_2 and volatile hydrocarbon species from fragmentation reaction of the polyaromatic constituents [11].

Coconut shell can be used for fuel and it is a source of charcoal also. It may be noted that activated carbon synthesized from coconut shell is considered better in comparison to those obtained from other sources because of its mesoporous structure which make it suitable for its application in EDLCs as electrode material [12–14]. Further, after carbonization of coconut shell, the three dimensional coconut shell based carbon has a hierarchical porous structure which can provide a large surface area, high conductivity, well connected and highly ordered microstructure [15], which helps in ion transport by providing low resistance

* Corresponding author. Tel.: +91 9479333913; fax: +91 7544267011.
E-mail addresses: sktripathi16@yahoo.com, sktripathi16@gmail.com (S.K. Tripathi).

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Fig. 1. Schematic flowchart for the CST preparation.

pathways, hence expecting improved performance as an EDLC electrode.

In the present studies, we have reported the synthesis technique of chemically treated and activated coconut shell based activated charcoal (CST) and its application as an electrode material in EDLC. The synthesized activated charcoal was characterized using N_2-adsorption–desorption isotherms, scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). EDLC cells have also been fabricated using optimized composition of blend polymer electrolytes comprising of polyvinylidene fluoride-co-hexa-fluoro propylene [PVdF(HFP)]–polymethyl methacrylate [PMMA]–sodium thiocynate [NaSCN]. Galvanostatic charge–discharge, ac impedance spectroscopy, cyclic voltammetry (CV) was used to characterize the EDLC cell.

2. Experimental details

2.1. Preparation of blend polymer electrolytes

PVdF(HFP) with an average molecular weight of 1.3×10^5 (Sigma–Aldrich), PMMA with an average molecular weight of 1.2×10^5 (Sigma–Aldrich) and inorganic salt NaSCN (Loba Chemie) were used in the present study. All the chemicals were dried before use. A solution-cast method was used to make polymer blend electrolyte films. Different composition of NaSCN, PVdF(HFP), PMMA were dissolved in DMF (Merck) and mixed together. The resultant solution was stirred and heated continuously at 60 °C for 10 h until the mixture gets homogenous and becomes gelly in nature. The optimized composition of polymer blend electrolyte used in the present studies is [PVdF(HFP) (80 wt.%) – PMMA (20 wt.%)] (80 wt.%) – [NaSCN (1 M)] (20 wt.%).

2.2. Preparation of biomass based charcoals and activated charcoal

A schematic flowchart for CST preparation is given in Fig. 1. Coconut shell as a precursor material was obtained from the Guna district, Madhya Pradesh, India. Clean the coconut shell from other materials such as coconut fiber or soil. Sun dry it for 2–3 days. The dried coconut shell was then kept in muffle furnace at 300 °C for 5 h. Soak this charcoal in chemical solution $CaCl_2$ (25 wt.%) for 18–20 h to become activated charcoal. Wash this activated charcoal with double distilled water. Now keep the samples in oven at 110 °C (overnight) for drying. Chemical activation has been widely used to obtain porous activated carbons with very high surface areas. KOH as an activating agent is one of the most effective agents employed for organic materials. KOH is mostly preferred over other activating agents because it causes more localized reactions with the carbon precursor and is more effective for highly ordered materials [16]. The chemical reaction between KOH and carbon during activation proceeds as:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$$

The reaction is then further continued by decomposition of K_2CO_3 and/or reaction of $K/K_2CO_3/CO_2$ with carbon. Chemical activation using impregnation method has been given elsewhere [17].

2.3. Construction of electrodes used in the experiments

The electrodes were prepared by making slurry of prepared activated charcoal powder and PVdF-HFP in the ratio 90:10 (w/w) in a common solvent acetone by thorough mixing. Fine films of electrodes were coated by spraying the slurry on carbon cloth (Ballard, USA) and kept in oven at 70 °C for 10–12 h.

2.4. Instrumental details

SEM observation was taken with the help of JEOL Model-JSM 6380LA. Nitrogen adsorption–desorption isotherms were measured at 77 K using Autosorb-1 Quantachrome Instruments, USA. X-ray diffraction (XRD) measurements were carried out using X' Pert PRO, Panalytical, Netherlands, using an operational voltage of 40 kV and current of 40 mA, respectively. In order to have better understanding in the carbonization process, a thermogravimetric analyzer (Diamond TGA/DTA, Perkin Elmer Instruments, USA) was employed to monitor the volatile evolution behavior of CST in N_2 atmosphere.

2.5. Electrochemical measurements

The EDLCs were fabricated using CST electrodes with polymer blend electrolyte PVdF(HFP)–PMMA–NaSCN which was sandwiched between two symmetrical electrodes. The performance characteristics of the EDLCs were characterized by using ac impedance analysis, galvanostatic charge–discharge technique, linear sweep cyclic voltammetry and prolonged cyclic tests.

The ac impedance measurements for the characterization of EDLCs were carried out by using computer controlled LCR HI TESTER (Model 3522-50, Hioki, Japan) in the frequency range from